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Superparamagnetic-Like Behaviour in RE_2WO_6 Tungstates (Where RE = Nd, Sm, Eu, Gd, Dy, Ho and Er)

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The magnetization isotherms were used to study the superparamagnetic-like behaviour in polycrystalline (powder) RE_2WO_6 tungstates (where RE = Nd, Sm, Eu, Gd, Dy, Ho and Er). The magnetization isotherms of the majority tungstates under study revealed both the spontaneous magnetic moments and hysteresis characteristic for the superparamagnetic-like behaviour with blocking temperature $T_B \approx 30$ K except the Sm_2WO_6 and Eu_2WO_6 compounds.

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1. Introduction

The magnetic and electrical measurements carried out on the RE_2WO_6 (where RE = Nd, Sm, Eu, Gd, Dy and Ho) tungstates showed a paramagnetic behaviour for samples with RE = Nd, Gd, Dy and Ho and more complex ones for samples with RE = Sm and Eu in the temperature range 4.2–280 K and an insulating state at room temperature [1]. A fitting procedure of the Curie–Weiss law, eliminating the temperature independent contribution from the experimental susceptibility data, showed a negative contribution (diamagnetic) for Nd_2WO_6 and a positive contribution (paramagnetic) for Gd_2WO_6, Dy_2WO_6 and Ho_2WO_6. It also indicated that a temperature independent paramagnetic contribution was favoured by the RE_2WO_6 compounds with a higher atomic number. However, in all compounds RE_2WO_6 the Landau, Pauli and van Vleck contributions were present but in different proportions so that different signs appeared as they could not be separated [1].

Doped and undoped rare-earth metal molybdates and tungstates are host candidates for luminescent applications. They are used for a fabrication of white light-emitting diodes showing high stability, energy-saving and safety [2, 3]. Thus, the main purpose of the present work is an attempt to study in more detail magnetic isotherms and correlate them with formation of the sub-micron sized particles or nanoparticles with the stable magnetization vector as the RE_2WO_6 tungstates under study are the paramagnetic powders.

2. Experimental details

The magnetization isotherms were measured in the zero-field-cooled (ZFC) mode and in external magnetic fields up to 14 T and at 4.2, 10, 15, 20, 30, 40 and 60 K using a step-magnetometer. RE_2WO_6 (RE = Nd, Sm, Eu, Gd, Dy, Ho and Er) were synthesized by a solid-state reaction between RE_2O_3 and WO_3 mixed at the molar ratio 1:1. The RE_2O_3/WO_3 mixtures were heated in the following cycles: 800 °C (12 h), 900 °C (12 h), 1000 °C (12 h) and 1100 °C (2 × 12 h). A routine phase analysis was conducted using a DRON-3 diffractometer run with Co K_α radiation ($\lambda = 0.179021$ nm). Diffraction patterns were collected over 12–60° 2θ at a stepped scan rate of 0.02° per step and a count time of 1 s per step. For the indexing procedure diffraction patterns were collected using a X'Pert PRO Philips diffractometer at the stepped scan rate of 0.02° per step and a count time of 10 s per step [4].

3. Results and discussion

All these tungstates have two futures in common: both zero coercivity and remanence. Figure 1 shows spontaneous magnetization without hysteresis loop for Nd_2WO_6. With increasing temperature a transition to the ideal paramagnetic state is observed. Figure 2 shows a non-cooperative magnetism for Eu_2WO_6 arising from spontaneous moments which are identical and located in isotropic surroundings, sufficiently separated to be independent of the others' existence. Similar behaviour was observed for Sm_2WO_6, not shown for clarity. Figures 3 and 4 reveal spontaneous magnetization with hysteresis loop for Gd_2WO_6 and Er_2WO_6. Above 60 K a transition to the ideal paramagnetic state is observed. Similar behaviour was also observed for Dy_2WO_6 and Ho_2WO_6, not shown for clarity. The small values of magnetic moment for Sm_2WO_6 and Eu_2WO_6 may be connected with the fact that the narrower multiplet widths, comparable

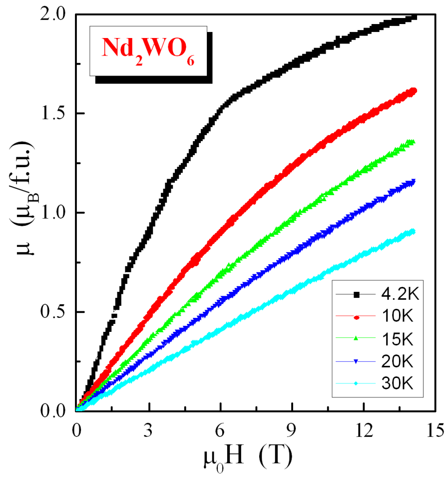

Fig. 1. Magnetic moment μ vs. magnetic field μ_0H for Nd_2WO_6 at 4.2, 10, 15, 20 and 30 K.

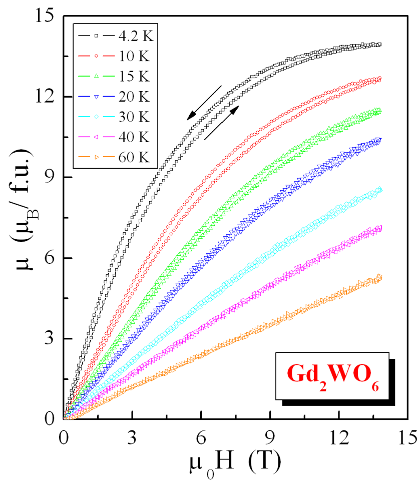

Fig. 3. Magnetic moment μ vs. magnetic field μ_0H for Gd_2WO_6 at 4.2, 10, 15, 20, 30, 40 and 60 K. A run of magnetic field is indicated by arrows.

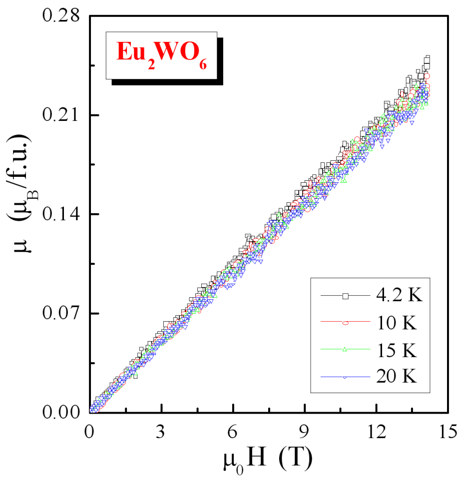

Fig. 2. Magnetic moment μ vs. magnetic field μ_0H for Eu_2WO_6 at 4.2, 10, 15 and 20 K.

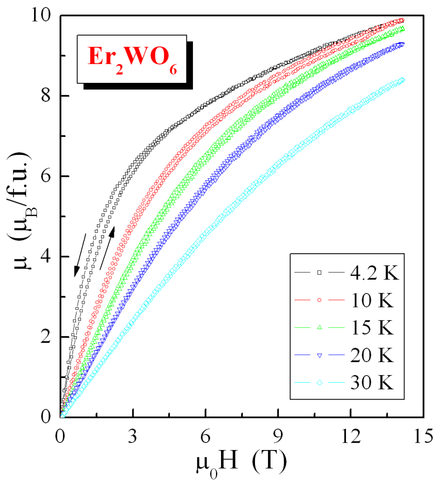

Fig. 4. Magnetic moment μ vs. magnetic field μ_0H for Er_2WO_6 at 4.2, 10, 15, 20 and 30 K. A run of magnetic field is indicated by arrows.

to kT, occur in the case of samarium and europium [5], so that not all the atoms are in their ground state [6]. Such levels above the ground state may not contribute to the magnetic moment [7].

No hysteresis in the non-linear dependence of $\mu(\mu_0H)$ and the universal function of μ_0H/T [8] (Fig. 5) characterise superparamagnetic-like behaviour for the finely divided Nd_2WO_6 material into sub-micron sized particles with fluctuating magnetization vector among the easy directions of magnetization. In the case of the Gd_2WO_6, Er_2WO_6, Dy_2WO_6 and Ho_2WO_6 tungstates the hysteresis occurs and the fluctuations of the magnetization vector among the easy directions of magnetization are blocked. In other words, the hysteresis both with zero coercivity and remanence is a consequence of an appearance of the stable magnetization of a single domain particle and the temperature at which this occurs is called the blocking temperature (T_B) [8]. For the tungstates above mentioned T_B does not exceed 30 K. In our case the blocking temperature may be equivalently defined as the temperature at which the hysteresis loop disappears.

The nature of hysteresis occurring in Figs. 3 and 4 may be connected with the uniaxial anisotropy [9] coming from the spin–orbit coupling driven from the Brillouin fit of the Landé factor [1] and the anisotropy distribution of the electron density. When the system involves magnetic moments with an easy magnetization axis the anisotropy energy reaches minimum. The value of the anisotropy energy defined as 1/8 of the area of the hysteresis cycle, whatever its shape [9] decreases with increasing temperature. The hysteresis width is the largest for the Gd_2WO_6 with the f^7 configuration and slightly decreases when it tends to f^{11}, i.e. for Er_2WO_6.

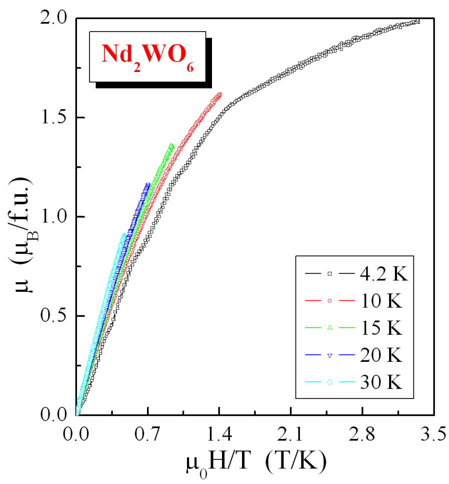

Fig. 5. Magnetic moment μ as a function of $\mu_0 H/T$ for Nd_2WO_6 showing superparamagnetic-like behaviour.

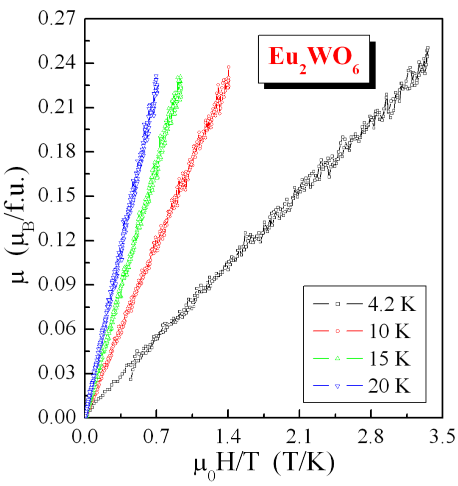

Fig. 6. Magnetic moment μ as a function of $\mu_0 H/T$ for Eu_2WO_6 showing ideal paramagnetic behaviour.

Figure 6 shows the magnetization curves $\mu(\mu_0 H/T)$ for the Eu_2WO_6 tungstate for that the universal function of magnetization, $\mu(\mu_0 H/T)$, is absent indicating only a paramagnetic state with the strongly reduced magnetic moment.

4. Conclusions

We have measured the magnetization isotherms in the ZFC mode of the powder RE_2WO_6 tungstates. The results showed a paramagnetic state for tungstates with samarium and europium and the superparamagnetic--like behaviour with fluctuating magnetization vector for Nd_2WO_6 as well as with the blocked magnetization vector for Gd_2WO_6 and Er_2WO_6 below 30 K. The hysteresis loops with zero remanence and coercivity indicate that the powder tungstates under study seem to be formed as the ferromagnetic single-domain particles not interacting between them.

Acknowledgments

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